Synthesis of Environmental Friendly Biochar and (Nano-Composite) for Sustainable Agriculture from Agro-Waste

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Dedication

This thesis work is dedicated to my Late Father Dr.Muhammad Zamin Khan, my mother, respectful teachers throughout the Masters Degree, and the fellows of NUST specially Bilal Sarfraz whom helped me throughout the project work and to all the research students whom aim to make PAKISTAN a better country for the future.

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Abstract

Agro-Waste WS was used to produce precious organic BC fertilizer products cost-effectively along administering it. The char created using agro-biomass waste was used back for agriculture which makes it more suitable to develop crop productivity & decrease environmental concerns of usual fertilizers. Moreover this char helps recover the soil due to its near to 7 pH, adding of higher quantity of carbon and lesser SI properties.

The research work focuses on synthesis of BC into an advanced enhanced BC manufactured material followed by testing if the BC produced from WS could soak up nutrients & also be a support material for discharging of micro and macro nutrients for the crops on slow releasing basis. Biochar and Nano-char were prepared by pyrolysis at two dissimilar temperatures following fusion of nutrient into the WBC via impregnation method. Both nano-biochars were identified by FT-IR, BET, XRD, SEM/EDX and TGA. Properties such as Ultimate analysis and proximate along other factors were also calculated using standard control guidelines. Experiments were also done on Water Retention, WA, SR and EWC for all biochar samples; results were compiled and evaluated for the best char. SLS performed displayed release model of some of the macro and micro nutrients for extended periods which is significant to plant growth & its yield.

In general the experimental data exhibited that biochar is a high-quality material however the BNC has better results, an environment friendly product which could be utilized as a possible fertilizer via slow liberation for green and sustainable agro processes.

Keywords:, *Nano-Biochar, Slow Release Fertilizer, Micro-Macro Nutrients, Wheat Straw Biochar, Sustainable Agriculture.*

Table of Contents

List of Figures

List of Tables

List of Abbreviations

WBC	:	Wheat Biochar
WNBC	:	Wheat Nano-biochar
WS	:	Wheat Straw
EDX	:	Energy-Dispersive X-ray
EWC	:	Equilibrium Water Content
FT-IT	:	Fourier Transforms Infrared Spectroscopy
SI	:	Salt Index
SR	:	Swelling Ration
SRF	:	Slow Release Studies
SEM	:	Scanning Electron Microscopy
TGA	:	Thermal Gravimetric Analysis
PA	:	Proximate Analysis
UA	:	Ultimate Analysis
WR	:	Water Retention
WA	:	Water Absorbance
XRD	:	X-ray Diffraction
BC	:	Biochar
FBR	:	Fixed Bed Reactor

Chapter 1

Introduction

1.1. Background

In the late 20th Century, the word of ‘biochar’ was originated as a result of derivation of two Greek words, Bios which meant life and char which was a form of a carbonaceous substance. This matter is carbon loaded substance is formed when dissimilar waste biomasses are burnt in a restricted furnace in incomplete or no source of oxygen known simply as pyrolysis[1].

However the manufacturing history of BC; can be addressed back to hundreds of years in Amazon basin, where among the tribes a practice of enclosed smoldering biomass with soil in pits and trenches. Biochar that we know of in the modern world has been used since centuries. The merging of charcoal into the earth to enhance the quality of the soil has been an old agricultural practice for many thousands of years on the planet [2]. Pre-Columbian people were mixing organic and inorganic residues with the soils known as Terra Preta today - rich in both organic matter & nutrients. The oldest depiction of charcoal use in farming maybe from the 17th century Encyclopedia of Agriculture by Yasusada Miyazaki, where the author cited an even older textbook from China. From there it can be known that rice husk charcoal was used as a soil improvement product possibly since the origination of rice farming in Asia. [3]

During the last decade, biochar importance has been on the rise due to its significance in climate improvement &agricultural profits among world environmental experts, agriculturists and policy makers. A product which is emphasized for its carbon sequestering properties, storage and soil amendment features[4].

Inter-related with the swift increase of the worldwide population, peaking overall energy supply is observed since the start of the 21st century and is anticipated to rise through 2040[5].One of the major challenges in today’s engineered earth is the massive giving out of greenhouse gases [6] which has considerable undesirable effects on the atmosphere including air pollution [7] and climate change [8]. Moreover the use chemical fertilizers have unquestionably played a fundamental part towards escalating the agricultural productivity over past half century [9] but the excessive use of these chemicals and fertilizers have backfired in recent times resulting in exhaustion of soil organic matter and nutrients along drop off in agricultural productivity especially in the tropical regions worldwide[10]. The solution to all these problems in recent times has been the use of biochar which has turned out to be quite a novel approach having probable benefits to both the atmosphere of the earth and sustainable agriculture.

The term "sustainable agriculture" is defined as the amalgamation of organic, chemical, physical, environmental, financial and social sciences in an inclusive way to build up new agricultural practices that are secure and do not make our environment worse[11]. In recent times on such product which has become the epitome of sustainable agriculture is the Biochar. It application at present is considered as a use of improving the quality of the soil and fertility to yield more crops, while being an environment friendly product itself providing ecosystem facilities such as control of contaminants[12] along the sequestering of carbon in huge amounts hence mitigating the climate. [13]

1.2. What is Biochar?

Biochar is dark black colored, vastly porous, very light weight, and have a pretty large surface area if they are grinded properly. Most of the composition is composed of C where as the remaining elements consists of N_2, H_2 and O_2. The remaining percentage consists of nitrogen, hydrogen and oxygen among other elements. However depending on the composition of biochar varies with different feedstock and process conditions. A carbon-rich firm product formed by heating biomass (mostly waste) with limited or no oxygen [14], the substance exhibits a spongy carbonaceous arrangement, functional group, and an aromatic surface. The thermal degradation processes used for the production of biochar consists of pyrolysis, carbonization and gasification.

A product which has so many applications in the modern world, from altering the physio-chemical properties of the soil [15] to decreasing the nitrogen emissions [16] to improving the nutrient availability along reduce nutrient leaching in the soil [17] and above all increasing the overall yield and productivity of crops [18]. In addition, biochar can sequester carbon in huge amounts where as they could also enhance the bioremediation of pesticides and chemical fertilizers through different applications maintaining the quality and fertility of the soil. Applications for biochar increase by the years and research indicates the number is on the rise for this special product.

1.2.1. Physical Properties

1.2.1.1. Surface Area

Surface area for any product a catalyst, or a simple biochar product is a very important parameter because this factor contributes to the adsorption of materials [19]. Results have indicated that Surface Area of BC can be augmented if the operating conditions mostly the temperature of the pyrolysis is increased from 250 to 500 °C, this consequently increases the specific surface area and microspores formation in the biochar. Escalating temperature from 250 to 600 °C amplified the surface area from 0.56 to 14.1 $m^2\ g^{-1}$ in sugarcane bagasse based biochar[20]. At another instance the surface area at 700 °C was 420 $m^2\ g^{-1}$ as compared to 6 $m^2\ g^{-1}$ at 300 °C for soya bean based biochar[21].

Furthermore the type of feedstock also affects the specific surface area. The surface area of biochar manufactured from bagasse was around 202 $m^2\ g^{-1}$ where as for coco-peat it was merely just 13.7 $m^2\ g^{-1}$[22].The possible explanation for this is the release of the volatile matter inside the feedstock as a result of the presence of cellulose and hemicelluloses during the process of pyrolysis and the temperature at which the pyrolysis takes place which increases the formation of the spongy structure and the specific surface area of the specific biochar. [23].

1.2.1.2. Surface Functional Group

Biochar has functional groups on the exterior (oxygen based) mostlyaccountable for the adsorption of a certain BC. Such groups play a pivotal role and are dependent highly on the temperature conditions during the process of pyrolysis .According to research the hydrogen and oxygen quantity, along the hydrogen to carbon ratio generally shows a decrease when pyrolysis is performed out at elevated temperatures. Another research study shows that the amount of surface groups within the biochar diminished with increase of pyrolysis temperature which was further supported through the results of Fourier transformed infrared (FTIR) spectra.

1.2.1.3. Biochar Stability

In the modern world BC is increasingly used and recognized worldwide as a very significant product for long-standing soil amendment however the stability of this product mainly is because of the kind of raw waste material& the temperature range of pyrolysis. Experiments have identified some types to degrade rapidly in soil while others take much more time hence the conditions of pyrolysis and the type of feedstock are two parameters which can be manipulate with to produce a certain much stable biochar type. Though, experiments suggest that increasing the temperature during pyrolysis increases the stability of biochar however much work is to be done to produce the most prized biochar yet which has if not the best stability but much better and improved stability overall.

1.2.2. Chemical Properties

1.2.2.1. pH

pH of BC is vastly erratic it mostly depends upon two things; pyrolysis operating settings & feed type. Both these contribute to a large set of data for the ph of biochar. Table 1 shows the pH of various crop residue char substances produced at different temperature settings.

Table 1: pH of different biochar feed

Feedstock	**Temperature/◦C**	**pH**	**Remarks**	**Refs**
Crop residues				
Corn Cob	600	10.1	-	[24]
Corn Stover	300-600	7.33-9.95	Increasing the temperature shows that the pH increased.	[25]
Wheat Straw	200 300	6.00 7.55	Wheat straw was pyrolyzed at three different temperatures however the	[26]

	500	10.19	results showed an increase in pH of the biochar with increase in temperature	
Sugarcane Bagasse	310-850	7.6-9.7	For Sugarcane the pH also increased as the condition of pyrolysis were increased.	[27]
Rice Straw	300-800	7.16-10.5	Both were first pyrolyzed at lower temperatures and increasing the temperature increased the pH of both the biochars	[28]
Rice Bran	300-800	6.89-10.9		
Rice Straw & Wheat Straw	300-500	7.7-10.4	For both the different type of feedstock's pH was increased when the temperature was increased.	[29]

Hence it can be concluded that for higher temperatures biochar with more alkaline properties as produced where as for low temperature pyrolysis procedures biochar with low acidic ph can be manufactures. Globally the ph of soil varies from country to country so some places higher ph biochar is preferred where at some place low pH biochar maybe suitable for the amendment of the soil.

1.2.2.2. Cation Exchange Capacity

The C.E.C is a calculation of its capability to maintain positively charged ions (Ca^{2+}, K^{+})[30].A property which contributes to the fertility of soil, the higher the CEC of certain soil the more cationic nutrients it can hold in greater quantities for a longer period of time than a certain soil which has a lower CEC, preventing leaching of nutrients and increasing their availability for the crops uptake. CEC of biochar depends on three factors the feedstock type, temperature conditions for pyrolysis and aging time. It is a vital property in association to the fertility of any soil. Higher the CEC of soil the more it can hold cationic nutrients in greater amounts and for a much longer period of time as compared to lower CEC soil, ultimately preventing the loss of nutrients along increasing their availabilities for plant growth.

1.2.2.3. Electrical Conductivity

Electrical conductivity is an imperative parameter of soil salinity. The higher the electrical conductivity of biochar more it improves the salinity of the soil due to nutrients such as calcium and magnesium which ultimately is harmful for the plants. Hence it is imminent to manufacture biochar having much low electrical conductivity (EC). From research electrical conductivity directly depends upon the Ash contents. More the ash content in a feed more is the electrical conductivity of the biochar. Ash contents of biochar are highly erratic due to two main reasons, types of feedstock and the conditions of pyrolysis So work should be done to produce biochar which has optimum content of Ash and have enough other nutrients such as potassium, phosphorous and sodium.

1.2.3. Agriculture Benefits of Biochar

One of the few problems faced by current agricultural procedures globally is the managing of excess amount of organic matter waste; otherwise it can lead to pollution, giving off of greenhouse gases and soil erosion [31]. As a solution most technologies are working to convert this waste into biochar and use it for agriculture applications to both manage and use the waste. Soil is the major factor in the field of agriculture the better the soil the better the crops and the better the yield. Studies exclaimed that the appliance of biochar on soil improves the soil in every aspect. Table 2 illustrates the Assets of soil and the influence BC have on it when used.

Table 2: Physical and Chemical Properties of Soil and their effects through use of Biochar

Soil	**Affected Property**	**Effect**	**Refs**
Physical Properties	Bulk Density & Porosity	Reduction in the bulk density of soil and increased porosity due to the application of BC	[32]
	Color	Changes in the overall color of the surface of the soil after the use of biochar.	[33]
	Water Retention	Water retention also increases since addition of biochar into the soil decreases the average size pore hence such small pores are able to hold more water due to the	[34]

		porosity	
	Compaction	Reduction of soil compaction by the addition of biochar into the soil along promoting of increased wheat vegetative growth	[35]
	Penetration Resistance	Biochar showed promising results reducing penetration resistance of sandy loam soils	[36]
	Infiltration	Results demonstrate that adding biochar to the soil, Improved the Infiltration factor by reducing it.	[37]
Chemical Properties	pH	The alkalization of the soil was increased through the use of biochar which increased the soil's pH	[38]
	Cation Exchange Capacity	Adding of biochar showed that it enhanced the capacity of C.E.C of the soil	[39]
	Total Organic C	Addition of biochar showed increased organic C to the soil without the presence of biochar	[40]
	Nutrients(Na, K, P, Ca etc)	Presence of BC in the soil elevates the accessibility of the different nutrients to the plants.	[41]
	Interchangeable Acidity	The addition of biochar to the soil showed promising results, reducing the interchangeable acidity	[42]

This shows that the addition of biochar to soil is very effective for every aspect of the soil and the crops to be grown in that soil, in return this leads to the improvement of crop production. Improvement in the productivity of soil via the increase of carbon content in the soil directly leads to increased yield of the crops. Also Cation Exchange Capacity is clearly elevated due to the use of biochar which elevates the amount of nutrients available for the plants which makes the plant healthier, makes the soil more fertile and increases the overall performance of the soil.

1.2.4. Composition of Ligno-cellulosic Materials Residues

1.2.4.1. Cellulose

A polysaccharide with of a linear chain of β-1, 4 linked D-glucose units with a degree of polymerization starting from numerous hundreds to over several thousands, which is the most plentiful organic polymer on planet earth. Due to its polysaccharide structure, a large quantity of hydroxyl groups exists along the backbone of the cellulose matter.[43]Sugar molecules that are attached together forming long chains that give wood its good strength. It is the major component of plant cell walls. It is used mainly in textile, paper and pulp industries. Cotton is pure form of cellulose. Cellulose; a complex natural lengthy string polymer prepared by the attachment of smaller monomers. The two monomers are the Beta Glucose molecules. When two monomers combine they give disaccharide which is also known as cell-biose. Cellulose is a polysaccharide made by combination of many cell-biose molecules combining in the same way as the small monomers. The cellulose contains mostly polar OH groups. They are usually hydrogen bonds containing OH groups on adjacent chains, building the chains together. Moreover cellulose has a relatively low enzymatic hydrolysis rate.[44]The formula of cellulose is $(C_6H_{10}O_5)_n$. A polysaccharide consist of straight chain of hundred to over thousands linked B-glucose molecules.

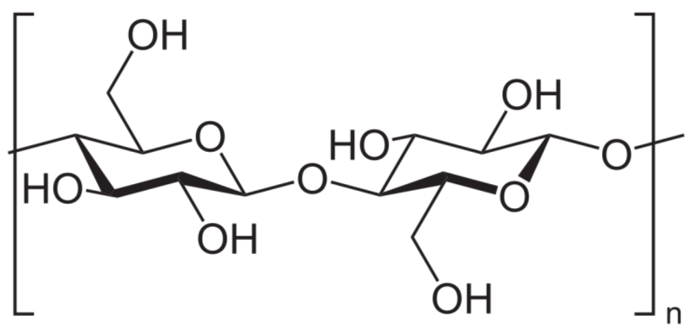


Figure 1: Cellulose compound diagram

Cellulose is tasteless & odorless, it is also unsolvable in water and along many solvents, but it can be decomposed (biodegradable).Cellulose properties are dependent on its degree of polymerization, the number of glucose units that make up one polymer molecule.

1.2.4.2. Hemi-cellulose

Is a hetero-polymer, simpler structure than cellulose which is composed of numerous polymerized mono-saccharides like aldohexose, mannose, galactose, etc It is produced from sugar nucleotides in cell’s Golgi apparatus. It is the major component of plant cell wall embedded in it and second most important element in the composition of wood. Hemi-cellulose is also known as polyose.

The general formula of hemi-cellulose is $C_5H_8O_4$.

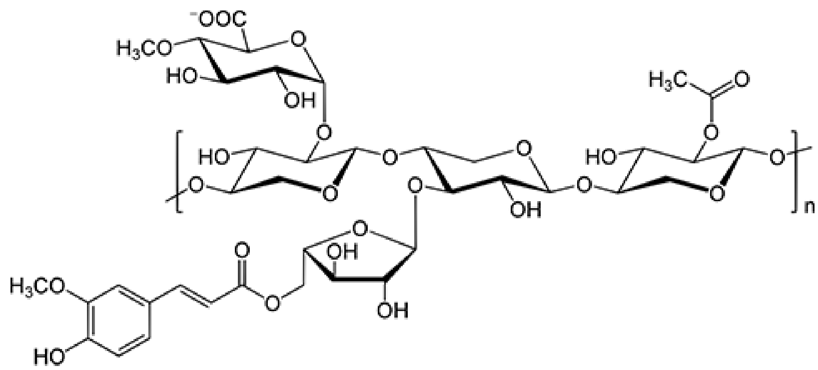


Figure 2: Hemi-Cellulose compound diagram

Hemi-cellulose is a branched structure rather than straight chains (500-3000 sugar units. The structure of hemi-cellulose is confounded and complex and is principally made out of a few unique kinds of different substance such as pento-ses along hexo-ses & glycolytic acid.

They are mainly condensation polymers (a molecule of H_2O is removed with every linkage).Polymerization degree (DP) of hemi-cellulose is also lower than cellulose i.e. 80–200 sugar units per hemi-cellulose molecule[45].Lower molecular weight &multi-branched. They are more soluble than cellulose and soluble in dilute alkali[46].Hemi-cellulose is white crystalline solid material and they are amorphous in nature and weak in strength.

1.2.4.3. Lignin

Is a complex natural heterogeneous polymer composed of phenyl propane units linked by ether bonds. It is composed of 63.4% carbon, 5.9% hydrogen, 0.7% ash, and 30% oxygen [47].It acts as a main component in the support tissues of terrestrial plants and some algae. Lignin is also the major component of plant's cell wall (makes 30% of plant's cell wall). It is also found in some quantities in in tracheids, vessels, fibres of xylem and phloem and sclerenchyma[48].Lignin is one of the most important and abundant organic and renewable resources on earth**.**

The general formula of lignin is $(C_{31}H_{34}O_{11})_n$

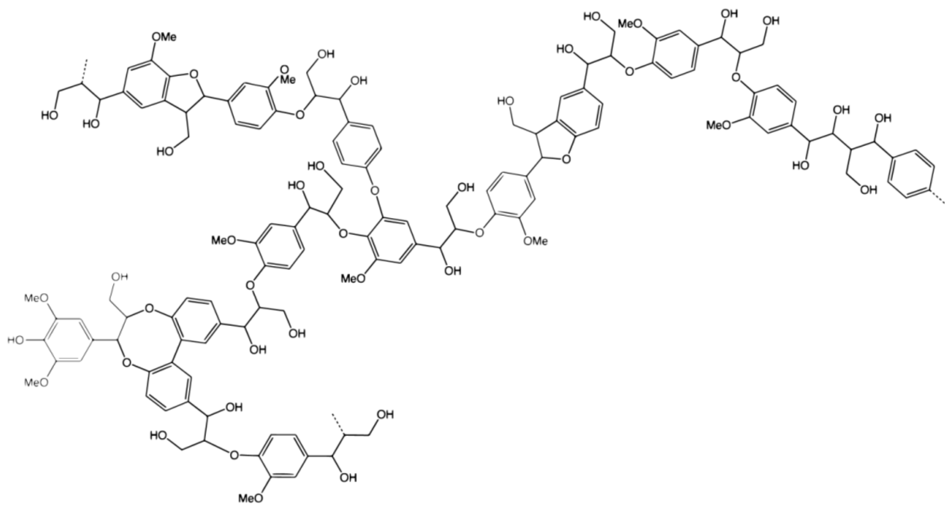


Figure 3: Lignin compound diagram

Lignin is a cross-linked phenol polymer. It is a three-dimensional heterogeneous polymer and aromatic structures. It is a branched molecule which is made up of phenol units and has strong intra-molecular bonding. Also water insoluble thus it shows a hydrophobic binding capacity. The molecular weight of Lignin is 1513.6 g/mol. It is chemically more stable and heat resistant than cellulose. The functional organic group of lignin includes COOH, OH, OCH_3. They are soluble in hot alkali and are easily oxidized but hydrolyzed by acids [49].The primary units of lignin molecules are p-coumaryl, coniferyl, and sinapyl alcohols. Usually occurs in yellow and light to dark brown color and are hard cannot be easily broken.

Following table 3 shows different agricultural waste products and their compositions respectively with most of them having cellulose, lignin and hemi-cellulose as the major constituents of agricultural waste by products.

Table 3: Agricultural residues and their compositions

Agro-Industrial Wastes	**Chemical Composition**					**Refs**
	Cellulose	**Hemi-Cellulose**	**Lignin**	**Extractives (%)**	**Moisture (%)**	
Corn Stalks	42.4	29.6	21.7	5.1	-	[50]

Cotton Stalks	43.0	25.0	30.0	2*	-	[51]
Rice Straw	42.7	30.9	20.3	6.1*	-	[52]
Sugarcane Bagasse	40.7	23.7	26.8	8.6	-	[53]
Wheat Straw	45.1	30.2	17.3	1.2	9.1	[54]
*By difference						

1.3. Biochar preparation from different feedstock via Pyrolysis

Studies and publication reveal that parameters such as type of feedstock (organic in this case) and the conditions for pyrolysis which include the temperature , inert conditions , the heat rate, time also affect on the properties of the BC that is produced through it. These factors can be termed as those which are very crucial in determining whether the biochar manufactured would be viable for the restoration and remediation or the soil or not. Hence, all these factors would conclude whether the biochar produced will or will not enhance the growth among the crops growth also increase the yield. Through literature it is imminent that temperature is one of the most important factor and it is what defines the physical & structural uniqueness of engineered biochar. Simple ways to produce biochar is through pyrolysis and carbonization using tube furnace , muffle or any other type of reactor, varying heating rate along the total time for the process using different organic feedstocks and reactors while temperature ranges from 300-700◦C along absence of oxygen.

1.4. Other Biochar Applications

- To Clean the Atmosphere: Biochar is additionally used to absorb natural, organic and inorganic noxious poisonous harmful substances and heavy metals from the atmosphere.[55]

- In mitigating Greenhouse Gases: The biochar stored in soil helps in the arrangement of ecological and agricultural benefits by reducing the green house gases and ozone harming substance discharge.[56]
- Used in Energy Production: It also has a key part in the energy invention.[57]
- Reducing CO_2 from Environment: Tremendous increase in amount of atmospheric amount of CO_2 i.e green house gases which prompts the global warming despite of the struggle and efforts made to lessen this environmental change. To avoid the most exceedingly awful results of environmental change, we have to fundamentally decrease global warming emissions and the contribution percentage of CO_2 is 55%. So, expelling out existing carbon dioxide from the atmosphere helps to reduce the increase in temperature.
- NO_2 Reduction from Atmosphere: The majority of Earth's atmosphere (78%) nitrogen. Nitrogen is present in the environment in a wide variety of chemical forms including organic nitrogen, ammonium (NH^{+4}), nitrite (NO^{-2}), nitrate (NO^{-3}), nitrous oxide (N_2O), nitric oxide (NO) or inorganic nitrogen gas (N_2). N_2O is a powerful greenhouse gas and the most important ozone depleting compound present in our atmosphere. It's affect on climate change is 298 times stronger than carbon dioxide. The major contributors of N_2O emissions from soil are the three processes of nitrogen cycle.
    1. Nitrification
    2. De-nitrification
    3. Nitrate Ammonification
- Mitigating CH_4: Biochar amendment may indirectly reduce CH_4 emissions by altering soil properties, such as soil pH, or other influencing factors. It suppresses CH_4 emissions by increasing soil pH while influencing microbial activities.[60]
- Used in Biogas Production: By adding biochar to a fermenter's biomass particularly heterogeneous biomasses, the methane and hydrogen yield is expanded, while simultaneously reducing CO2 and ammonia. By adding biochar to biogas slurry nutrients are also protected and away from the harmful emissions.[61]
- In Rice production: There have been several studies which show that the adoption of biochar is significant for rice production.[62]other uses include that Biochar is also

used in Industrial materials such as carbon fibers and plastics. It is used in electronics such as semiconductors and batteries. Often used in Cosmetics including soaps and skin-creams and in industrial paints and coloring as well.

1.5. Objectives

Waste biomass is derived to produce valuable biochar product and is characterized to produce nano-biochar enhancing its chemical and physical properties which is further used as a soil amendment product. The aim of this valuable product is to reduce leaching of nutrients; improve soil properties & prevention of chemical fertilizers and to recycle biomass through an effective process and manage it efficiently.

Other indirect objectives can be preservation of landfill space & fossil fuels while also having revenue generated from waste. Finally being an agricultural country, turn the waste into useful, profitable products such as Biochar and to help with the energy crisis & economic conditions of developing countries.

Chapter 2

Literature Review

2.1. Section 1

Paper 1: Review of biochar for the management of contaminated soil: Preparation, application and prospect.

Preparation: Biochar was prepared at 200-900°C via thermal disintegration without the presence of oxygen, called as pyrolysis. Convention process results in high char productivity However char characteristics are affected by diverse parameters including raw material, retention time, heat rate and temperature.

Factors affecting biochar:

1. Feedstock, Temperature and Retention time.
2. Gas flow rate/pressure.
3. Additives and Activation/modification.

Paper 2: A systematic review of biochar use in animal waste composting.

Preparation: Biomass was pyrolyzed at higher temperatures of (300–650◦C) without the presence of oxygen. The overall process outcome was the creation of a carbon-rich rock-solid result (biochar), along bio-oil, and gas such as Carbon dioxide, Methane etc. Amongst the range of techniques engaged (Table 4), slow pyrolysis is deemed as the central procedure for biochar manufacture.

Paper 3: Food waste to biochars through pyrolysis: A review.

Preparation: Biomass was taken and pyrolyzed at temperatures of 400–500 °C while applying a heat rate of 0.1–1 °C/s, the residence time for the overall process was from 5min to 30 min. Slow pyrolysis is very important since this procedure produces maximum char as compared to fast pyrolysis.

Paper 4: Synthesis and characterization of environmental friendly corncob biochar based nano-composite – A potential slow release nano-fertilizer for Sustainable agriculture.

Preparation: Corncob Biochar was synthesized via conventional pyrolysis technique. Bought locally and then washed, dried in open air &grinded. They were then taken to a reactor for slow pyrolysis procedure at temperatures of around 400 °C for almost a residence time of 6 h with nonstop source of N_2 at of 1 L hr^{-1}.

Paper 5: Pyrolysis of wheat straw in a thermo-gravimetric analyzer: Effect of particle size and heating rate on de-volatilization And estimation of global kinetics.

Preparation: Using DuPont 951 Thermo-gravimetric Analyzer (TA Instruments, Inc., USA) along a platinum pan pyrolysis was carried out, Temperature of 800◦C was used with the particle size between 0.15mm-0.35mm, nitrogen gas was utilized as the inert gas with flow rate of 45 cm^3/min while heat rate set in the range of 5 to 20 ◦C/min, particle.

Table 4: Slow Pyrolysis Literature Study

Sr.No	**Temp/◦C**	**Residence Time**	**Heating Rate/◦C/min**	**O_2 Presence**	**Ref.**
1	<600	300-550s	1-10	No	[63]
2	300-650	5min-12hrs	10-30	No	[64]
3	400-500	5-30mins	0.1-1◦C/s	No	[65]
4	300-400	6 hrs	-	No	[66]
5	800	-	5-20	No	[67]

2.2. Section 2

Pyrolysis is the process where lingo-cellulosic substances such as agricultural wastes can be converted into value product via thermal decomposition under inert state provided to the substance specifically in an O_2 scarce atmosphere. The biomass agricultural waste consists of 3 main materials i.e. cellulose, hemicelluloses and lignin. Cellulose and hemicelluloses carry high levels of hydrogen and oxygen while Lignin contains high levels of carbon as compared to the other two constituents[68].The word pyrolysis is formed from two different words where pyro is defined as fire while lysis specifically means breakdown into fundamental parts. The technology is fairly old and was used earlier in different areas globally as well as Europe and present Gulf countries to produce the product of charcoal which was an essential product in the old times[69] and now in the modern times its used mostly to produce bio-oil as well which can be mixed with gasoline to produce a hybrid fuel. [70]so the objective of pyrolysis in the modern world is to reuse the waste materials such as agricultural waste to yield good quality esteemed energy materials replacing the non-renewable fuels, manage the waste, improve the environment and control the climate changes.

This thesis focuses on the use of slow pyrolysis which is useful for the production of good quality charcoal using increased residence time but low temperatures along low heating rates. The residence time is usually around half hour at the maximum. Maximum biochar is produced in slow pyrolysis. Furthermore studies disclose that factors such as type of feedstock also have a control on the properties of the biochar that is produced through pyrolysis. Through literature it is on the cards that temperature is one of the most imperative attribute and it is what defines the physical & structural exclusivity of modified biochar[71].Table 5 also shows the low, mid and high levels and factors of pyrolysis where as Table 6 shows the use of slow pyrolysis to produce biochar and products taken from literature throughout the years.

Table 5: Pyrolysis Parameters and Factors Affecting

Factors	**Levels**			**Ref**
	Low	Mid	High	[72]
Temperature(◦C)	300	400	500	
Residence Time(s)	3600	5400	7200	
Mass of Biomass (g)	125	250	500	
Heat Rate (◦C/min)	5	10	20	

Table 6: Conventional Pyrolysis of dissimilar feedstocks performed using different experiment conditions.

Feed Stock	Mechanism/Product	Temp /◦C	Time	Heating Rate ◦C/min	O_2	Ref.
Rice Hull	Rice hull was placed inside a muffle furnace, operating conditions were provided.	350	6h	-	Low	[73]
Dry Biomass (Animal Waste)	Slow pyrolysis was carried out to form a carbon rice solid product (biochar).	300	5mins	10	No	[64]
Corn Biomass	Inert conditions were achieved in a tube furnace using nitrogen for the pyrolysis to take place.	400	3h	5	No	[74]
Corn Cob	Simple pyrolysis was carried out in a slow burn using nitrogen for the inert conditions to produce biochar.	300	6h	-	No	[66]
Wheat Straw	The waste is placed in a ceramic pot, which is then taken to the muffle furnace, conditions were provided to obtain biochar.	300.	6h	10	Low supply	[75]
Rice Straw	Using a stainless steel autoclave the feedstock was valorized providing the operating conditions to produce biochar.	450	3h	3	No	[76]
Food waste	Waste was pyrolyzed in a furnace via slow pyrolysis to produce the product biochar.	400	5-30mins	0.1-1◦C/s	No	[65]
Wheat and corn	Samples were precisely weight and pyrolyzed to obtain biochar	300	60mins	10	No	[77]

Walnut Shell	The Sample was heated from ambient temperature to the final temperature to fabricate biochar	400	-	10	Low supply	[78]
Olive Mill Waste/ Oak Acorn shells/ De-seeded Carob pods	Feedstock off all three materials was placed in the crucibles which were heated further in an electrical muffle furnace to manufacture the biochar.	300-400	1.5hr	-	Low supply	[79]
Poultry litter and swine manure	At first the raw materials was place in stainless steel cylinders following by placing them in the furnace to obtain the different biochars.	300, 400	1hr	10	No	[80]
Wheat and Rice Straw ,Corn Cob	Slow pyrolysis at the specific temperatures was carried out to manufacture the specific biochar	300, 350, 400, 450	1hr	20	No	[81]
Softwood sawdust Lignin	The process was carried at a lab scale via slow pyrolysis to product biochar	300, 500, 650	8hr	5	No	[82]
Wheat Straw/ Wheat Hust	Thermal pyrolysis was carried out at the different temperature to product different products including biochar.	300, 350, 400, 450	1hr	25	No	[83]
Rice Straw	Slow Pyrolysis was performed to enhance the process.	200, 250, 300	2hr	3	-	[84]
Peanut/Cotton/Sorghum stalk,	Pyrolysis was performed using fixed bed reactor	700	5mins	10	No	[85]
Rice Straw, Forest biomass Pine	The pyrolysis of the agricultural wastes were completed in a nitrogen based F.B.R	350-500	1hr	20	No	[86]

Chapter 3

Methodology

In the project, Biochar is produced from waste agriculture wheat straw by pyrolysis method. In which the wheat straw was cut down into small pieces and passed through 0.63mm mesh screen. The biochar produced was then stored. Moreover the biochar produced was then used to produce Nano-composite of the biochar via impregnation. The more detailed process is given below.

3.1. Raw Materials

Given below are the raw materials that were used during this project or process.

- Wheat Straw
- Distilled Water (H_2O)
- Chemicals

3.1.1. Synthesis of Wheat Straw Biochar

Wheat Straw (WS) was produced via conventional pyrolysis (slow) process. The raw wheat straw was acquired from Swabi District, it was washed, dried in the sunlight and then it was crushed via a grinder into smaller size, less than equal to 0.63mm. The crushed wheat straw was put in tube furnace for slow pyrolysis with temperature range of 300–400 °C for 30mins with incessant resource of N_2 to keep inert surroundings during the whole process producing Wheat biochar (WBC) as the product. After heating, it was chilled with nitrogen, keeping flow rate intact. BC was put in a sample bag zipped and labeled accordingly.

Figure 4: Synthesis of WBC from WS

3.1.2. Chemicals

Zinc Sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$), Magnesium Sulphate Heptahydrate ($MgSO_4 \cdot 7H_2O$),Potassium chloride (KCl), Sodium Phosphate monobasic Dihydrate ($NaH_2PO_4 \cdot 2H_2O$) Calcium-Phosphate ($Ca_3 (PO_4)_2$), Ferrous Chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), were purchased from Sigma Scientific (Pvt) Ltd. Sodium Hydroxide (NaOH), Hydrochloric acid (HCl), Sodium Chloride (NaCl), Sodium Nitrate ($NaNO_3$) and nitric acid (HNO_3) were provided by SCME. 5% solution of each salt/chemical was prepared via simple dilution where 5g of each salt/chemical was added in 100ml of distilled water in a beaker, stirred and then poured into a plastic bottle to be stored. These solutions were later on used in the impregnation technique to add macronutrients & micronutrients to the biochar to form nano-char composites.

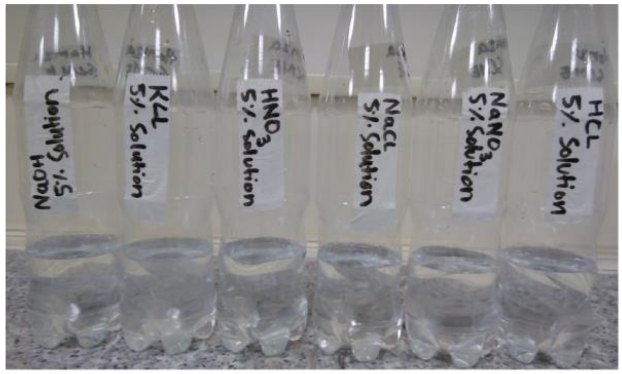


Figure 5: Chemical Solution Part A

Figure 6: Chemical Solutions Part B

3.1.3. Synthesis of Wheat Nano-Biochar Composite

The biochar produced via slow pyrolysis was taken put in a conical flask to produced nano composite of the wheat biochar. The process used to produce the composite is known as impregnation method where the biochar is put in the flask , distilled water is added to the biochar and then 5% solution of the salts mentioned in the chemicals section were all poured into the flask. The resulting contents were mixed and stirred for 4 hours with the help of magnetic stirrer so that maximum adsorption of all the salts added to the biochar could fuse well into the pores of the WBC. The substance obtained after 4 hours was sieved, dehydrated in oven at 105 °C for 10mins. Finally the latest new composite of the biochar was put in a sample bag for further use.

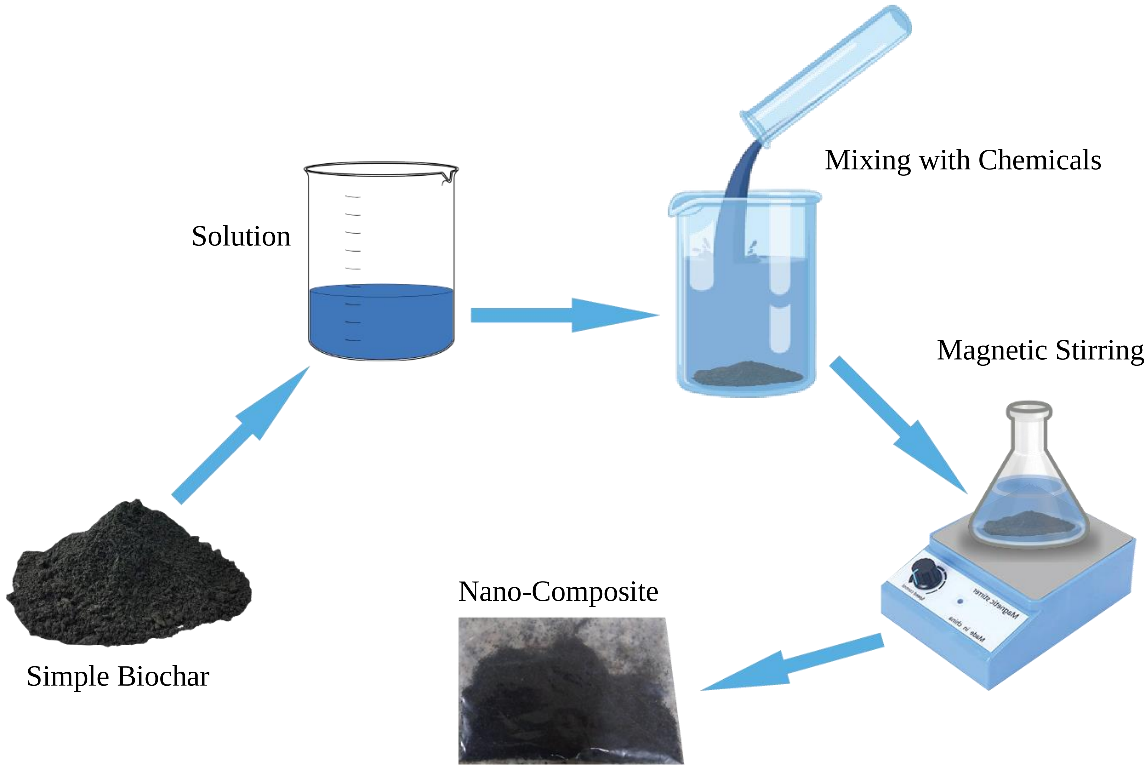


Figure 7: Synthesis of WBNC from WBC.

3.2. Physio-Chemical Properties Analysis

3.2.1. Salt Index

It is a numerical value which is expressed as a ratio among two solutions or substances where the chosen fertilizer product is compared to the same weight of Sodium Nitrate ($NaNO_3$). The chosen fertilizer is divided by the solution of Sodium Nitrate. Normally conductivities of either the mixtures or solutions are taken as the ratio to find the Salt index.[87]

In this study, 0.25 g of each WBC_{300}, WBC_{350}, $WBNC_{300}$, and $WBNC_{350}$, samples were placed in 4 glass beakers and 50ml of clean distilled water was put into all the beakers & mixed. Another 0.25 g of Sodium Nitrate was put into a beaker and 50ml of H_2O was added to it and stirred. All the five beakers were kept for 24 h. Conductivity of each sample of biochar was measured after 24 hours and the ratio of these conductivities compared to Sodium Nitrate was used to calculate the SI Index.

3.2.2. Swelling Ratio and Equilibrium Water Content

Swelling ratio for biochar is defined as increase in fractional weight following the adsorption of any solvent it is placed in over a period of time.

The Equilibrium moisture content (EMC) of a hygroscopic material can be defined as the point at which the biochar is neither losing any moisture nor gaining any moisture content when the biochar is placed in a moist environment. This parameter is dependent on air temperature in which biochar was place and the relative humidity around it. The values of both SR and EWC can be calculated by the equations below.[87]

$$\boldsymbol{SR} = \frac{\boldsymbol{Ws - Wd}}{\boldsymbol{Wd}} \tag{1}$$

$$\boldsymbol{EWC}(\%) = \frac{\boldsymbol{Ws - Wd}}{\boldsymbol{Ws}} \times \boldsymbol{100} \tag{2}$$

Where, W_s is the wet weight while W_d as the dry weight of char and nano-char respectively for all the 4 samples.

For this study, we took 0.25 g of each WBC_{300}, WBC_{350}, $WBNC_{300}$,and $WBNC_{350}$,and put them in 50 ml of distilled water, the samples were totally underwater and then left for 24 hours. After that they all were filtered with the help of Vacuum Filtration and reweighed again. The equations (1) and (2) were then used to find both the SR and EWC of the samples.

3.2.3. Water Absorbance Studies

A property which is mainly utilized to calculate the quantity of water that can be absorbed by any product. Some of the factors that affect water absorption include the type of product (what is the product made of), any addictives if added to the product, the temperature at which the product was manufactured and the residence time of the process.

For these experiments, 0.25 g of each WBC_{300}, WBC_{350}, $WBNC_{300}$,and $WBNC_{350}$ were taken & tagged as $\mathbf{W_1}$,Two Petri dishes were taken, and weighed then tagged as $\mathbf{W_2}$ (1 weighed as 51.206 g which was utilized for biochar at 350 °C while the second weighing 36.135 g utilized for biochar at 300 °C). The chars were put inside the dishes and they were placed inside the desiccators, water was added to the dishes to generate humid conditions for the biochars. Lids were tightened on the desiccators and the char samples were left for a few days inside the desiccators. Afterwards the dishes were taken out of the desiccators & they were re-weighed again and labeled as $\mathbf{W_3}$, to calculate the water absorbance ability of the four samples of the biochar. Equation (3) below was utilized to find the results for the WAS. [88]

$$\boldsymbol{WAS}(\%) = \frac{\boldsymbol{W3-W2}}{\boldsymbol{W1}} \times \mathbf{100} \qquad (3)$$

Where,

$\mathbf{W_1}$: Weight of sample of biochar
$\mathbf{W_2}$: Weight of two different Petri dishes
$\mathbf{W_3}$: Weight of sample + Petri dish after a few days in desiccators

3.2.4. Water Retention Studies

Water retaining in the soil can be termed or understood as the water that is retained by the soil granules when it flows through the gaps between the soils granules before this water either joining underground water streams or surface torrents. This is a very important factor for plants because more the retention in the soil more water will be available for the crops which consequently ensure more water for the plants uptake. In arid environment this can be a very serious parameter because every water molecule available for plant is imperative for their better development. Biochar can be utilized at such instances being porous in nature it can improve soil's water retention capabilities providing more water for crops for increased time and ultimately affecting their yields.

For this research, 0.25 g of each $WBNC_{300}$, and $WBNC_{350}$, samples were taken in 2 beakers and 12.5 g of polished soil was put into both the beakers tagging them as $\mathbf{W_{300s}}$ and $\mathbf{W_{350s}}$.A third beaker was filled with 12.5 g of refined soil which was the control for the experiment and labeled as $\mathbf{W_s}$. 7.5 ml of water was measure using a measuring cylinder and put into three beakers. Following, 24 h all beakers were re-weighed & the data was noted. They all were then shifted inside a glass container and re-weighed after 24 h for the next 15 consecutive days. Data was collected for over a period of 15 days and then graphs were plotted for all the three samples to study the water retention property for each sample. Equation (4) was utilized to compute the results for the 3 samples over the period of 15 days which is written as below:[89]

$$\boldsymbol{WR}(\%) = \frac{\boldsymbol{W2}}{\boldsymbol{W1}} \times \mathbf{100} \tag{4}$$

Where,

W_1: Preliminary Weight of Beaker on 1st day (soil + water),

W_2: beaker weight (soil + water) on 2nd Day & so on.

The same formula is used for the samples of biochar where W_1 is the preliminary weight of beaker having biochar, soil and water while W_2 is beakers weight on the second day & so on.

3.2.5. Slow Release Studies

These experiments were performed to check the liberation of the some of the specific nutrients from the modified biochars at 300 °C and 350 °C. Experiments were directed in one step; $WBNC_{300}$ and $WBNC_{350}$ were put into Tap water to observe the loss of specific nutrients model. They were carried for ten days inside a glass column; 2 g of bio-nano char was placed inside the glass column then 20 ml of the tap water was added to it. After every 24 h, 10 ml of water was taken from the column; the sample was tagged and after wards it was characterized to check the leak of the nutrients into the tap water.

To find concentrations of Nitrate along Phosphate ions, U.V visible spectrophotometer was utilized. Controlled calibration curves were plotted for both the ions using standardized solutions (200 mg, 400 mg, 600 mg, 800 mg and 1000 mg) Absorbance was noted and plotted as shown in Table 7 for nitrate and Table 8 for phosphate ions to find the values of slope and intercept for each ion using equation 5. The samples collected from the glass column were then analyzed for absorbance of phosphate and nitrate ions using the full spectrum of UV-Visible Spectrophotometer at different wavelengths for phosphorous and nitrogen. The values of absorbance and data of intercept, slope were used to find the concentration of the ions in the samples of water collected from the biochar glass column experiments. For K^+ and Na^+ Ions tap water samples were collected for 10 days as discussed and sent for analysis. Flame Photometer was used to characterize the water samples for the respective nutrients.

$$\textbf{Biochar (mg)} = \textbf{(Absorbance – Y-Intercept)} \div \textbf{(Slope from C.C)} \quad (5)$$

Table 7: Nitrate Salt Concentration (mg) Vs Absorbance (Au)

Nitrate Salt(mg)	**Absorbance(Au)**
0	0
200	0.0457
400	0.098
600	0.1493
800	0.1981
1000	0.2484

Table 8: Phosphate Salt Concentration (mg) Vs Absorbance (Au)

Phosphate Salt(mg)	**Absorbance(Au)**
0	0
200	0.1334
400	0.248
600	0.3683
800	0.4816
1000	0.5963

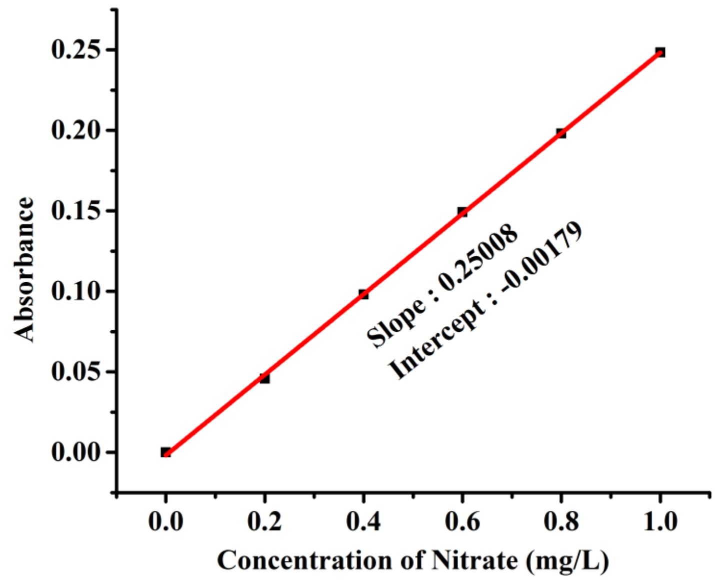


Figure 8: Calibration Curve of Nitrate Ion

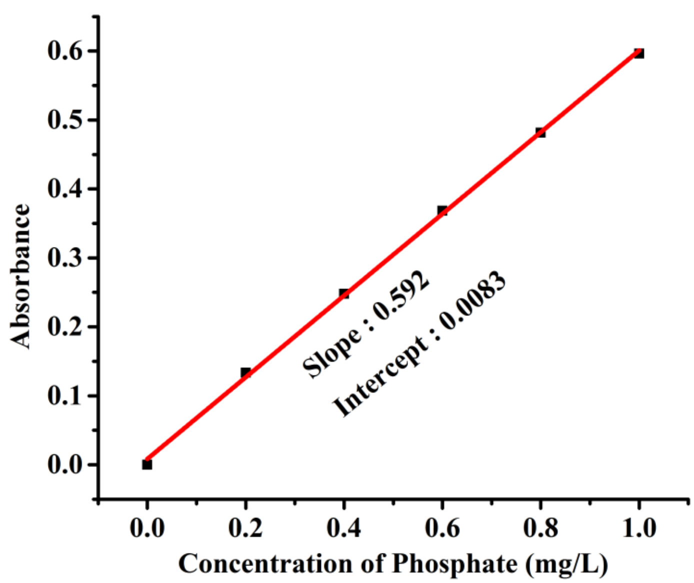


Figure 9: Calibration Curve of Phosphate Ion

3.2.6. Proximate, Ultimate and other parameters

PA is a method which is used to find out four unknowns of an organic substance; Firstly moisture content (ASTM E871-82) of any organic matter where the initial weight of a substance is taken and labeled W, it is then heated at 105 ˚C, after a few hours or a day; the substance is taken out and then re-weighed as W_1. Equation (A) is then used to calculate the moisture content which is as:

$$\boldsymbol{MC}(\%) = \frac{W - W1}{W} \times 100 \quad \text{(A)}$$

Where,

W: preliminary weight of substance,

W_1: weight after heating it at 950 ˚C.

Secondly volatile organic matter (ASTM E872-82) can be found via heating the organic substance at 850 ˚C for a few minutes in a Muffle furnace. The initial weight of the substance decreases hence using equation (B), the total (%) of volatile matter can be calculated:

$$\boldsymbol{MC}(\%) = \frac{W - W1}{W} \times 100 \quad \text{(B)}$$

Where,

W: preliminary weight of the substance,

W_1: weight after heating it at 950 ˚C.

For calculation of Ash (ASTM D1102-84) the organic substance is combusted at higher temperatures of around 650 ˚C until constant weight is achieved. Remaining contents were represented as Ash which mostly contains limestone, aluminum, silica, and other trace elements. Fixed carbon content is found by the difference of the parameters mentioned above which is as shown in equation (C).

$$\boldsymbol{FC}(\%) = 100 - \text{Ash} - \text{VM} - \text{MC} \quad \text{(C)}$$

Ultimate analysis is the technique which is used to find out the composition of elements inside an organic substance. The elements include Carbon, Hydrogen, Oxygen, Sulfur and Nitrogen The percentage of O (%) is calculated as a difference of Carbon (%) , Hydrogen (%), Nitrogen(%), Sulfur(%) and Ash(%) from 100.[90]

$$\boldsymbol{O}(\%) = 100 - \mathrm{C}(\%) - \mathrm{H}(\%) - -\mathrm{S}(\%) - \mathrm{N}(\%) - \mathrm{Ash}(\%) \quad \text{(D)}$$

3.3. Characterization Techniques

After biochar preparation and its physio-chemical analysis, it is decisive to characterize the biochar to recognize its chemical composition and morphology. The analytical techniques for biochar used in this study includes XRD, FTIR, Electron microcopy (SEM), EDX,TGA, Proximate and Ultimate analysis.Fig.10 presents the commonly used techniques for characterization of the biochar in this research.

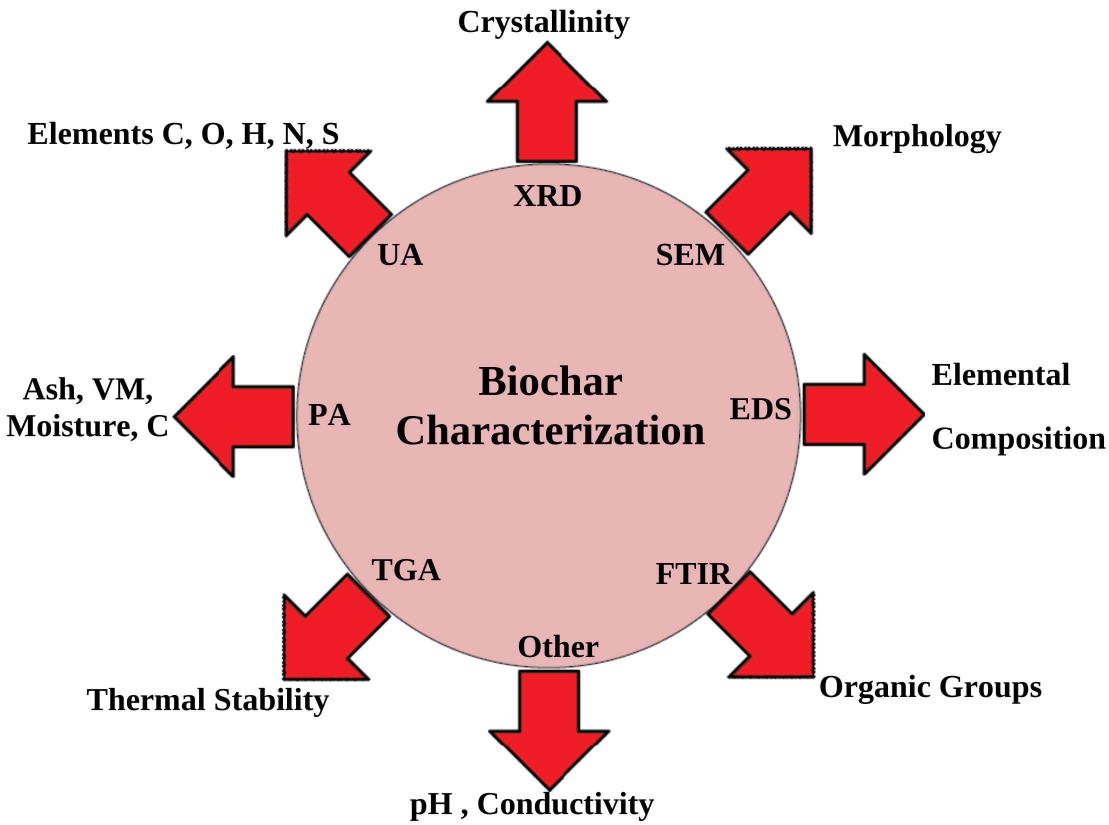


Figure 10: Different analysis methods

3.3.1. X-ray Diffraction (XRD)

- ***Working Mechanism***

A solitary crystal, when exhibited to monochromic X-rays, constructs diffraction maxima in agreement with law of Bragg's. The specific angle θ, the angle between the primary X-ray beam (with wavelength) and the family of lattice planes, with characteristic spacing d while n is an integer. In this technique, the incident beam, normal to the diffracting plane, and the diffracted beam lie all in a plane. These rays are concentrated by collimation on the specimen, which consequently results in constructive interference, which satisfy Bragg's Law. This can be written mathematically as below. Figure 11 shows the schematic of Bragg's Law

Mathematical Form: $\boldsymbol{n\lambda} = \boldsymbol{2dsin\theta}$

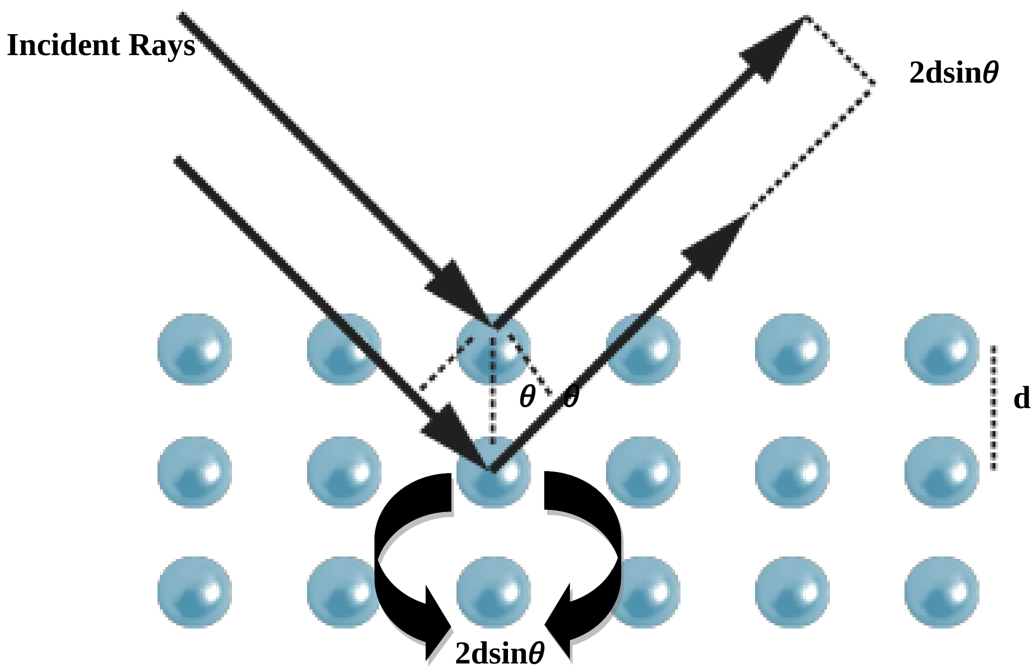


Figure 11: XRD Diagram

Where,

n: order of reflection,

$\boldsymbol{\lambda}$: represents X-rays wave-length,

d: The distance amongst two planes of atoms that give rise to diffraction peaks,

$\boldsymbol{\theta}$: angle created between incident beam& that normal to the lattice plane.

- ***Goals of XRD***

1. Characterization and identification of crystallinity of materials.

2. Determination of unit cell dimensions and average particle size.
3. It can also be used for the measurement of sample purity.
4. It can determine crystal structures and calculate the lattice spacing of substances.

3.3.2. Scanning Electron Microscopy (SEM)

It is one of the frequent methods for enhance imaging the micro-structure and morphology of the samples[91]Starting with the process, an electron beam with little energy is bombarded on the object which scans the surface of the material. During this process quite a few diverse interactions take place as the beam reaches and go through the exterior of the material, which directs to the release of photons and electrons from sample surface. Different detectors are present at the other end; depending on the type of material the image can be produced. Figure 12 illustrates some parts of SEM.

SEM consists of several components some of which are:

1. On the top is located the electron gun which emits electrons which are accelerated normally in the range of 0.1–30 keV.
2. The Electromagnetic lenses along the apertures which are used to spotlight and shape the electron beam so that it can focus on the center of the object or material.
3. Vacuum so that the electrons may not be disturbed by the air around or surroundings.

- ***Goals of SEM***

1. Surface Morphology of the sample.
2. Chemical composition of the material.
3. Topographic Information.

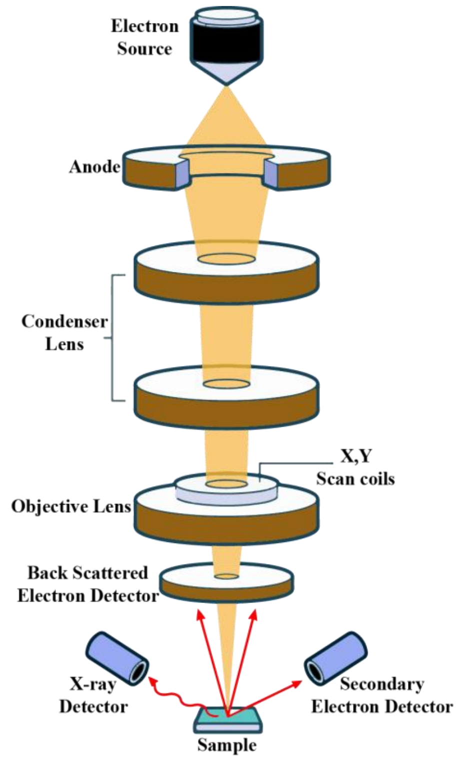


Figure 12: SEM Apparatus

3.3.3. Energy dispersive X-ray spectroscopy (EDX)

It is sometimes also referred to as EDX micro-analysis. This method is mostly utilized to find out the element makeup of materials or the elemental composition. The mechanism works as interface of several supplies of the rays' excitation & the object. Since every element has its own characterization peak it is easy to find out the peaks of all different elements.EDS consists majorly of three components which are linked to SEM and used to accordingly:

1. Emitter which radiates the X-rays.
2. Collector which collects the X-rays passed through the sample.
3. Analyzer detects and analyzes the results.

- ***Goals of EDX***

1. Find the elemental composition.

3.3.4. Fourier -Transform Infrared Spectroscopy (FTIR)

FTIR is also recognized as F.T.I.R Spectroscopy, it is an analytical method which is utilized to recognize polymeric, organic and in-organic substances. The technique employs infrared beam to scrutinize trial subjects for their chemical properties. It propels infrared radiation in the range of about 10,000 to 100 cm^{-1} throughout a substance, where some of it is cut through the sample while some is absorbed by the sample. For the absorbed radiation it is detected and presented usually from 4000 cm^{-1} to 400cm^{-1}, including molecular peaks images of the test samples. Every particle has its own unique peak which makes it easy to identify the molecules and their confirmation.

FTIR has the following fractions:

1. IR Source
2. Sample compartment
3. Detectors/Sensors/Amplifier
4. Processor

- ***Goals of FTIR***

1. Access the functional groups of the sample
2. detection of contaminants
3. Confirmation of new or unrecognized materials

3.3.5. Thermal Gravimetric Analysis (TGA)

It assesses weight alterations in a substance via temperature changes (or time) while is performed in a very well controlled procedure environment. Its standard uses comprise of measurement of a substance's overall thermal stability, moisture &solvent content, and the presence of certain contents inside a certain compound. The technique starts by steadily increasing temperature of a test material inside furnace while its weight is calculated via analytical balance which is remote from the furnace. Reactions including combustion can be found out through TGA since mass loss occurs during such reactions.

TGA mostly consist of these parts:

1. Controlling System
2. Furnace
3. Heating element
4. Sample transporter
5. Gas supply unit

- ***Goals of TGA***

1. Calculate material's thermal stability
2. Percent composition of component in a specific compound
3. Moisture content

3.3.6. Brunauer Emmett Teller (BET)

By this technique the precise exterior area (S.A) of a material can be measured along the pore range allocation of the sample. The detailed surface area of fine particles is calculated by physical adsorption. Gas molecules on the exterior of the solid sample are adsorbed. Then by finding the quantity of adsorbate gas equivalent to a mono-molecular coating on the exterior the specific area is found out. The determination of the specific area is generally performed at almost liquid nitrogen temperature. Gas adsorbed is calculated by a constant flow process.

BET components usually are:

1. Coolant Area
2. Drive Shaft
3. Sample Cell
4. Sensors

- ***Goals of BET***

1. Find out the aperture size allotment
2. Calculate Specific SA.

3.4. Statistical analysis

The research statistics and information was noted &developed using the software of MS Excel and Origin respectively. All factors were calculated as average of three replications of their respective experiments where as for the study of slow release, readings were adjusted in case of blank.

Chapter 4

Results &Discussion

4.1. Characterization Results

4.1.1. X-ray Diffraction (XRD)

The results of X.R.D of WBC & WBNC in the range of 2θ = 5 −65° were scanned, shown in Figure 13, They portray WS has reasonably high contents of carbon. Almost all samples demonstrate that biochars unveil a scattered peak at 22.37°, 22.14° and 22.72°, representing cellulose[94]. BNC at 350◦C being a more favorable biochar with low intensity peaks arise originating at 28.36◦[95] and 40.52◦ for only biochar and at 27.95◦ and 39.65◦ for the nano-char verifying carbonaceous arrangement of the sample. Evaluating all the samples together characterizes lead to the statement that the basic configuration of the char remains identical[96], however it can be seen that minor changes were observed in the intensities which proves the nutrient adsorption of the different nutrients into the core of the BC samples. JCPDS No. of each substance present in the biochar samples have been indentified for further study and correlation of results.

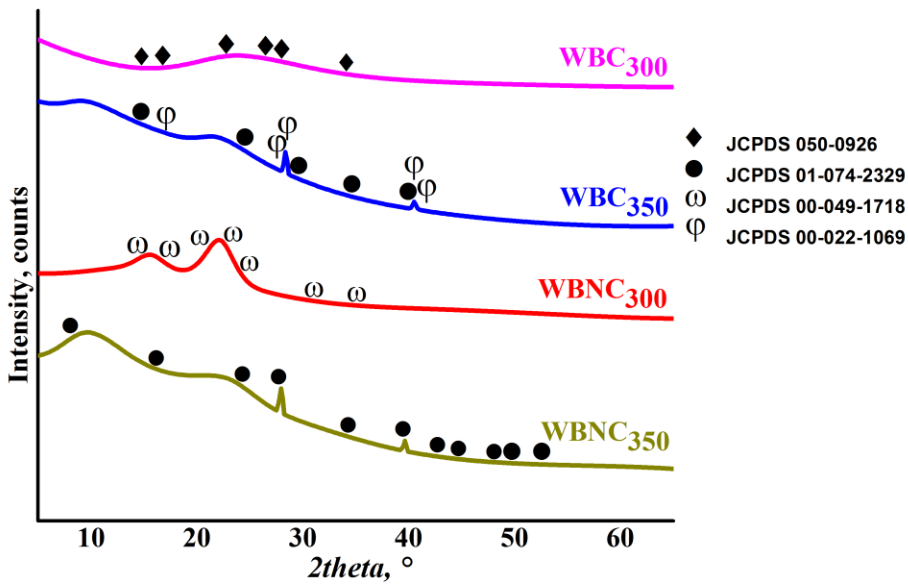


Figure 13: Powdered X.R.D Diffraction of WBC300, WBC350, WBNC300 and WBNC350 samples.

4.1.2. Scanning Electron Microscopy (SEM)

S.E.M gives detail about morphology of the derived wheat biochar and the modified nano-biochar samples (WBC and WBNC). Fig 14 represents the images of the samples at 300 ˚C captured at diverse resolutions of 500 µm (A, B) &1mm(C-H) while figure 15 represents the samples derived at 350 ˚C, all taken at resolutions of 1 mm. The images confirm the porous and spongy structure of the biochars and the WS-derived biochar at 350 ˚C demonstrates engorged and crumpled peripheral showing higher porosity at elevated temperatures, this is due to an effect of the liberation of volatile substances out of the biomass sample.[97]

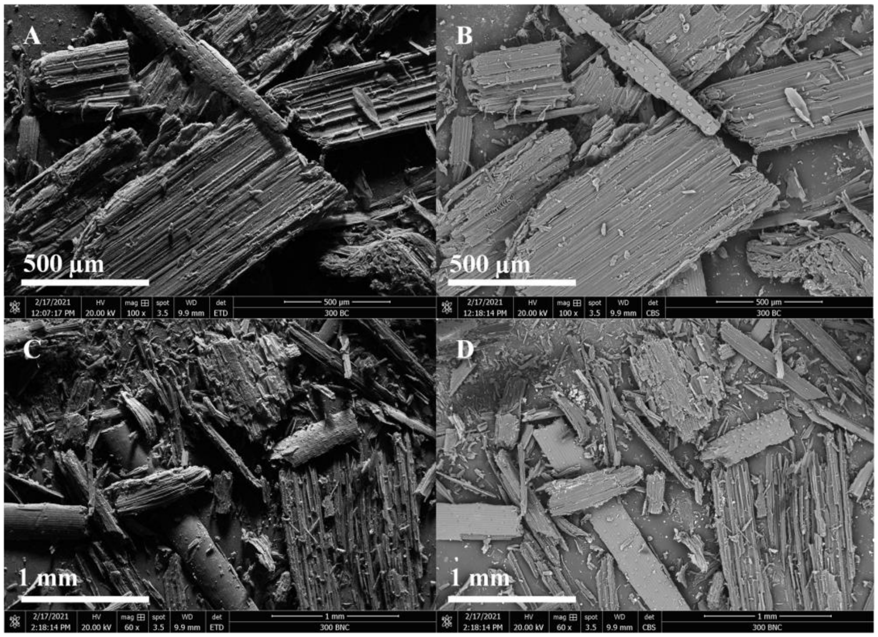


Figure 14: SEM imagery of WBC (A, B at 500µm resolution) &WBNC$_{300}$(C, D) at resolutions of 1mm respectively, showing porous and spongy structure of the samples.

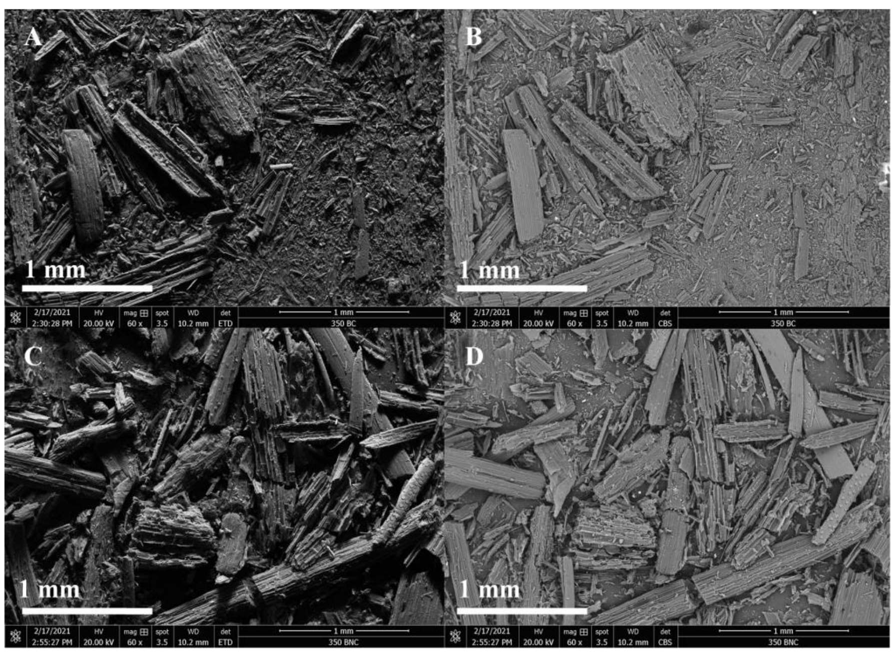
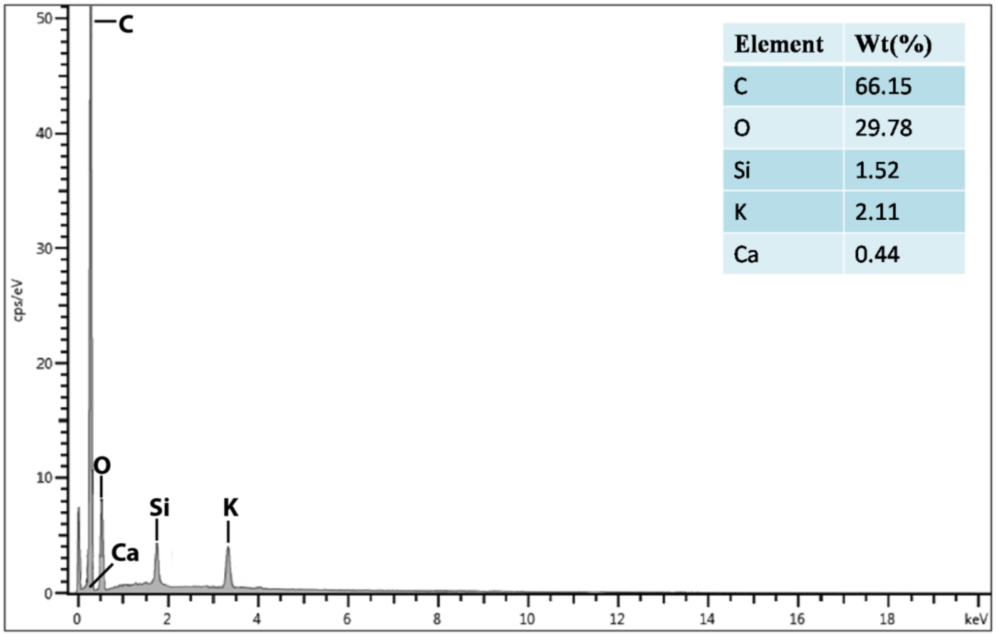


Figure 15: SEM imagery of WBC$_{350}$ (A-B&WBNC$_{350}$ (C, D) at resolutions of 1mm respectively, showing porous and spongy structure of the samples.

4.1.3. Energy Dispersive X-ray spectroscopy (EDX)

Elemental data analysis of char samples and customized biochars was carried out by EDX. Evaluating the figures evidently show and verify the impregnation of the micro &

macro nutrients into the array of the chars. FTI-R analysis confirms the difference of the all the elemental wt (%) of each ion depending upon their attraction with the arrangement of the BC along the carbon present while functional groups as confirmed by the analysis of FTIR. Figure 18 shows the mapping of the different nutrients.



Element	Wt(%)
C	66.15
O	29.78
Si	1.52
K	2.11
Ca	0.44

Figure 16: Elemental Data Analysis of WBC

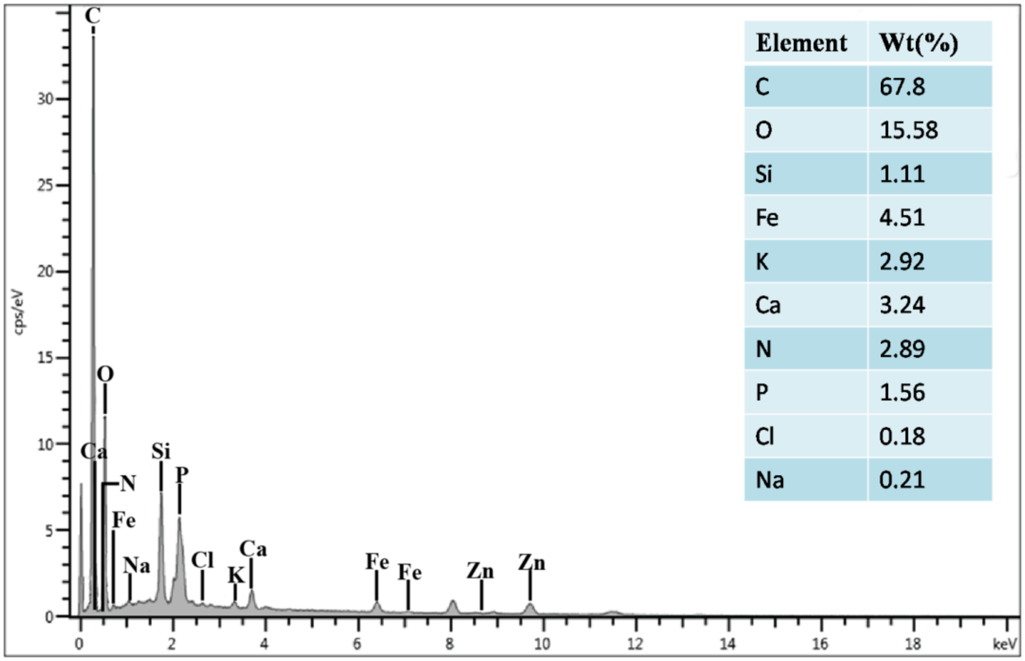


Figure 17: Elemental Data Analysis of BNC

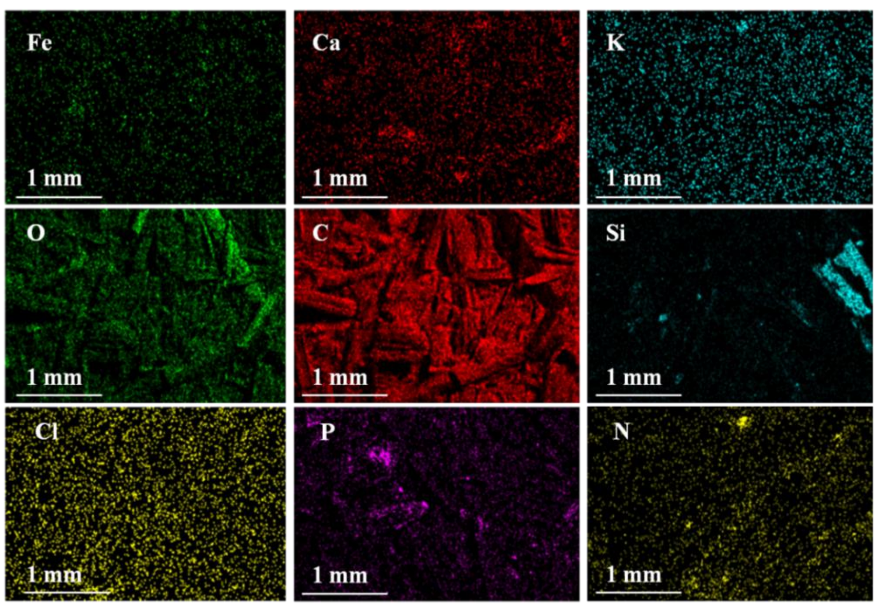


Figure 18: EDS mapping of the different macro and micro nutrients in the nano-biochars together, respectively.

4.1.4. Fourier Transform Infrared Spectroscopy (FTIR)

Biochar mostly is depicted as carbonaceous matter and a substance which has loads of oxygen functional groups such as (-COOH) & (-OH) groups on its exterior plane [98] along pores throughout its structure. To find these groups and confirm the impregnation of nutrients the biochar was characterized through FTIR analysis and studied. The characterization of biochars prepared at 300 ˚C and 350 ˚C were studied. In general, huge variety of the FTI-R curves amid WBC & WBNC were seen at 350 ˚C, which recommended that the groups were distorted after biological alteration. Fig 19 compared the FTIR spectra of all chars at 300 ˚C and 350 ˚C. Moreover the char produced had the major bands in the array 1000-1500 cm^{-1}, meaning presence of huge numbers of hydroxyl functional groups (-OH) along carboxylate functional bonds (-COOH) inside the char, such bonds are readily available to make complexes along metal ions [99]as confirmed in the curve of BNC_{350} with much development of new peaks. Also the peaks at 1621-1631cm^{-1}signify double C bond (C=C)aromatic ring while the range of 3425-3435 cm^{-1} confirms the Hydroxyl functional group (OH) on the outside surface of the biochar [100]which is because of the moisture content confirmed by Proximate analysis, so this spectrum should be allocated to the bonds of O-H stretching[101]. Moreover, a peaks at 500-800 cm^{-1} are assigned to groups such as FeO [102] and ZnO [103] indicating the impregnation of nutrients. Finally shifting peaks in all samples at 1092-1102 cm^{-1} authenticate incorporation of the salt ions into the porous structure of the WS char. [103]

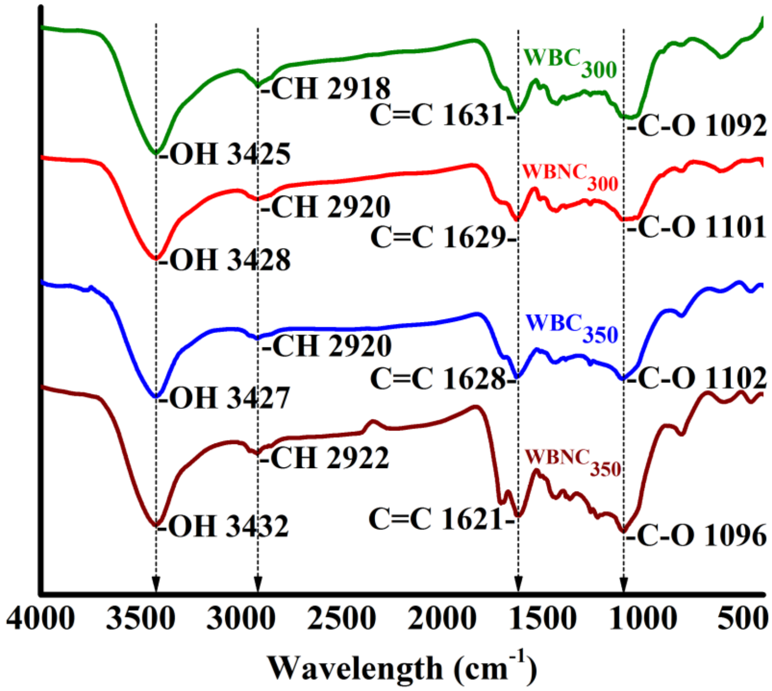


Figure 19: FTIR Spectra of WBC300, WBNC300, WBC350And WBNC350, Illustrating changes in peaks ofWBNC350, confirming the sorption of nutrients onto the Biochar sample.

4.1.5. Thermal Gravimetric Analysis (TGA)

TGA was performed to inspect thermal stability of WS and each derived and modified biochar. All lines in figure 20 specify early mass loss upto temperatures of 200-250 ˚C; this can be linked with removal of preliminary moisture content present in each of the samples as presented in Table 9. Early mass loss in WS shows combustion of carbon content along removal of volatiles depicting WS is less stable. Biochars produced at 300 ˚C is and 350 ˚C lose mass content on higher temperature portraying that they are more thermally stable. The second phase of weight loss for all samples can be observed between the temperatures of 200-500 ˚C which is certainly linked with thermal disintegration of the left over organic material inside the samples[104] and due to the emanation of gases[105].Exclusively, hemi-celluloses disintegrate in the limit of temperatures 200 to 300 ˚C, while the range of cellulose; which decomposes at 250 to 350 ˚C while lignin decomposes in the range of 200 to 500 ˚C, likewise[106].

Also each line keeps expanding after 500◦C verifying advanced thermal decomposition which could be as a result of fragile bonds (C–C) & (C–H), respectively.[107].

Roughly identical progression of decline was denoted in both the BNC curves (Figure 20) with slight variance amid simple biochars and modified biochars. The minor changes can be recognized because of the absorption of nutrients into the structure of the BC. In short, TGA authenticate firm nature of all the BC derived from the WS.

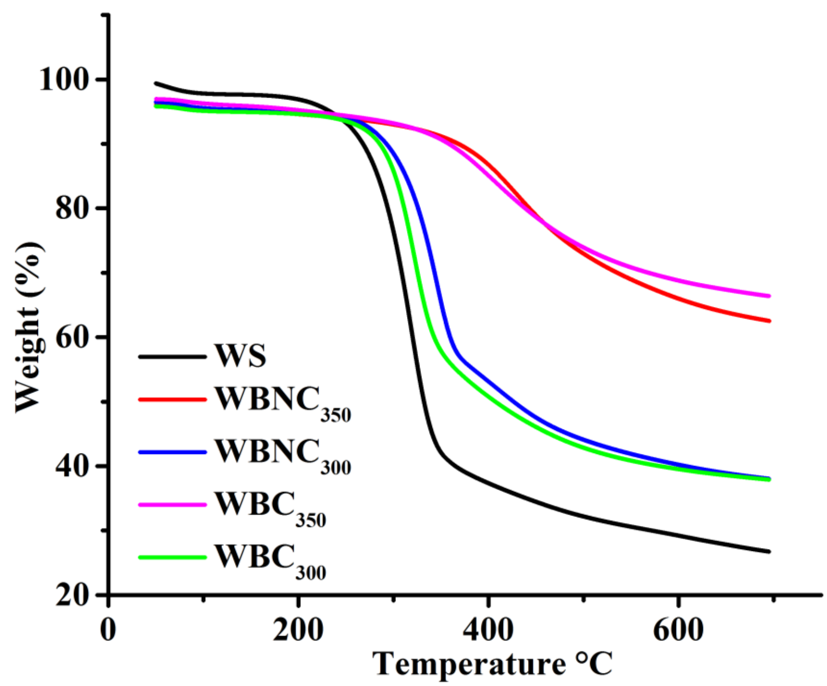


Figure 20: TGA analysis of Wheat Straw, biochar derived wheat straw; $WBNC_{350}$, $WBNC_{300}$, WBC_{350} and WBC_{300}.

4.1.6. Brunauer Emmett Teller Analysis (BET)

Synthesized Biochars were examined via nitrogen adsorption isotherms. S_{BET} was higher for both Nano-Biochar samples as compared to the simple biochars figure 21-22 illustrate the evaluation between each sample. The adsorption-desorption isotherm of all the samples observed; portray the blend of the Type-I & type-IV isotherm. The first sort of isotherm is a sign of the micro-porous character of the biochar while that of the fourth type isotherm indicates the coexistence of the micro-pores along meso-pores in the design of the samples [107].The wheat straw-derived Nano-biochars at 350 ˚C expressed comparatively decrease BET specific surface area (S_{BET}; 1.86 m^2/g) in comparison with Nano-biochar at 300 ˚C which had 2.87 m^2/g BET specific surface area. This is owing to the pore arrangement which are accountable for this value of S_{BET} since biochar is malformed at higher pyrolysis temperatures [108].

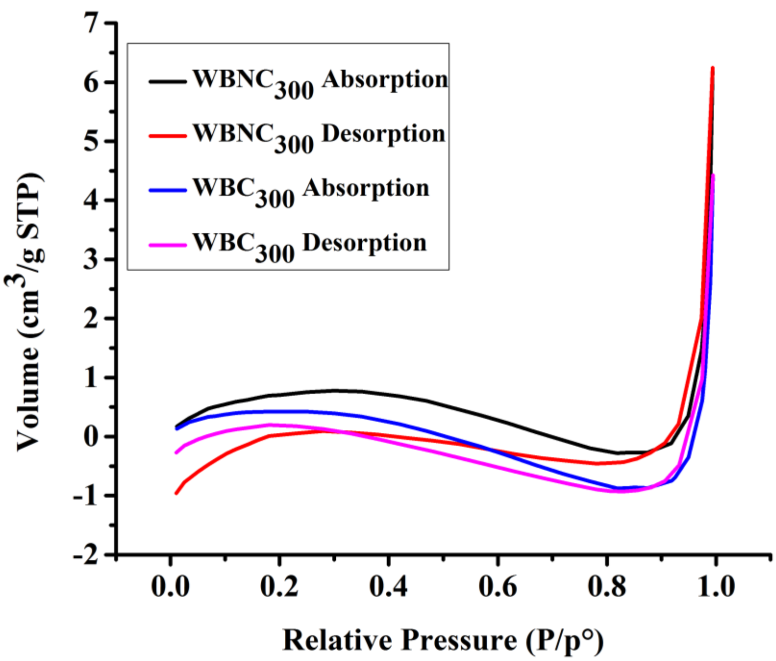


Figure 21: Structural Attributes of the Biochar and Nano-Biochars samples at 300 ˚C showing N_2 absorption/desorption isotherms

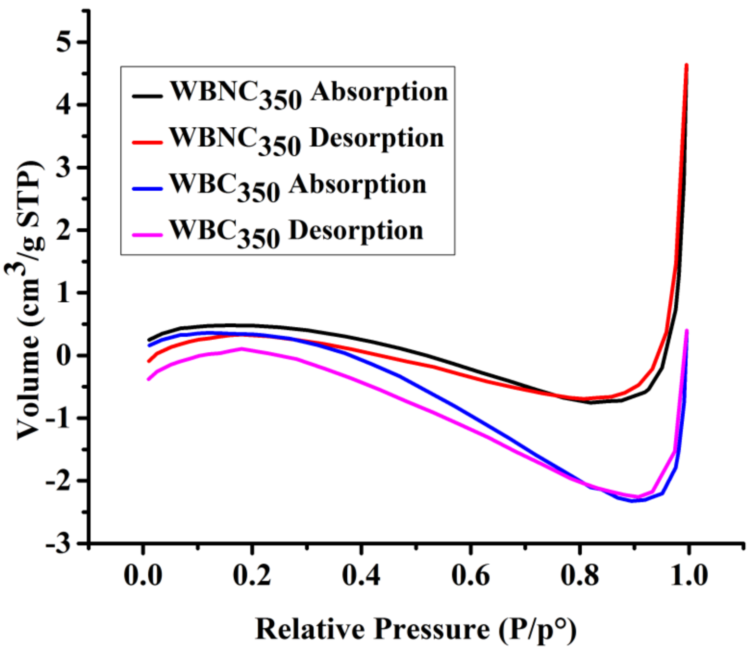


Figure 22: Structural Attributes of the Biochar and Nano-biochar samples at 350 °C showing N_2 absorption/desorption isotherms

4.1.7. Proximate Ultimate Analysis and Other Parameters

Proximate analysis, ultimate analysis and properties have been calculated for the raw WS, BC & BNC samples. Table 5 signifies all of the results for the evaluation of the samples. WS has elevated content of Volatile substance, moisture and Ash in contrast to the biochar. The samples have better carbon content because of the pyrolysis executed which removed moisture and volatile substances to some extent. More details in Table 9.

For the pH values of the three samples, WS is alkaline where as WBC has slightly alkaline pH however the BNC's pH turned out better and closer to the neutral pH indicating it as a good choice for agriculture use[109] Boost in Conductivity of WBNC supports the truth of sorption of the metal ions into the porous nature of the BC.

Table 9: Proximate, Ultimate and other properties of WS, WBC & WBNC350.

Property	**Wheat Straw**	**WBC**	**$WBNC_{350}$**
Volatile Organic Matter	66.8	37.2	39.41
Moisture Content	8.45	6.13	5.62
Ash Content	5.75	3.62	4.71
Fixed Carbon	19.1*	53.05*	50.26*
pH	8.91	8.11	7.22
Cd(%)	34.22	58.44	56.77
Hd(%)	5.68	4.67	4.92
Od(%)	60.1*	36.89	38.31
$Conductivity_{350}$ (μS)	-	84.7	228.2
$Conductivity_{300}$ (μS)	-	67.8	197.3
*by difference			

4.2. Soil Parameters and Slow Release Studies

4.2.1. Synthesis of WBNC

Slow pyrolysis was used to synthesis biochar at first and later on the biochar was turned into nano-composite biochar with the help of impregnation method since biochar generally has a porous nature so it supports the impregnation of nutrients to turn the simple biochar into modified nano-composite biochar. This ability can ultimately be utilized for slower release of all nutrients into deprived soil making biochar a much more sustainable fertilizer for the modern day sustainable agriculture applications.

4.2.2. Salt Index

Salt index is an imperative asset of any latest fertilizer product in the market. More its value among the fertilizer more is the fertilizer harmful for any kind of plant which therefore decreases the crop productivity. Hence it is central for any fertilizer to have the value of SI within the tolerable limit. SI of each sample of biochar came out pretty lower making it a friendly and better fertilizer to use for crops and also being a sustainable clean fertilizer.

Table 10: SI Values for Samples

Samples	Conductivity	Salt Index
BC_{300}	67.80 µs m^{-1}	0.016
BC_{350}	84.70 µs m^{-1}	0.021
BNC_{300}	197.30 µs m^{-1}	0.048
BNC_{350}	228.20 µs m^{-1}	0.055
$NaNO_3$	4.11 ms m^{-1}	-

4.2.3. Water Absorbance Studies, Swelling Ratio and Equilibrium Water Content

Using the equations (1) and (2) Swelling Ratio and EWC for all four samples was calculated where it was clearly examined with raise in temperature SR & EWC values also raise up. While comparing the simple biochar to the Nano-biochar , the composite biochars show increased values of both the factors with $WBNC_{350}$ having the maximum values of Swelling Ratio and Equilibrium Water Content and simple biochar at 300◦C has the lowest values for both the parameters. Whereas Table 12 has results for WAS calculated via the help of equation (3), it obviously illustrates that BC has the affinity to soak up water and the more the temperature at which it was prepared via slow pyrolysis the more can the product of biochar absorb water into its structure due to the porous and spongy nature. Hence easily soaking up water can is a good thing in arid situations in which there may be much lower water available. This characteristic can be used to supply water to the earth and aid in betterment of conditions for vegetation in the arid surroundings[92].

Table 11: Equilibrium Water Content & Swelling Ratio Tables

Samples	W_d(g)	W_s(g)	SR	EWC (%)
WBC_{300}	0.252	0.895	2.550	71.80
WBC_{350}	0.251	0.999	2.740	74.80
$WBNC_{300}$	0.255	1.090	3.270	76.60

$WBNC_{350}$	0.255	1.193	3.670	78.60

Table 12: Water Absorbance Studies

Samples	**W_1(g)**	**W_2(g)**	**W_3(g)**	**WC (%)**
WBC_{300}	0.252	36.14	36.27	52.0
WBC_{350}	0.255	51.21	51.37	61.0
$WBNC_{300}$	0.256	36.16	36.27	54.0
$WBNC_{350}$	0.252	51.21	51.37	64.0

4.2.4. Water Retention Studies

The Figure 23 below shows the table for WR studies which displays the three experiments first as soil control (having no BC), soil along $WBNC_{300}$ and the last one soil along $WBNC_{350}$. Water reduced among all three tests however when evaluated $WBNC_{350}$ showed it has higher WR capability, then came $WBNC_{300}$ & finally only soil had the least capability to retain water. WR is a considerable factor for the plant growth since it assists in retaining water in the soil for longer times which consequently helps the flora as they receive more water [93].

Table 13: Water Retention with Soil only, Soil & $WBNC_{300}$ and Soil & $WBNC_{350}$

Days	**Soil Control(±0.5)**	**Soil with $WBNC_{300}$(±0.5)**	**Soil with $WBNC_{350}$(±0.5)**
1	83.0	90.5	94.5
2	81.0	88.0	92.0
3	75.0	86.5	91.5
4	74.5	83.5	90.0
5	74.0	78.0	85.0
6	73.5	77.0	83.5
7	67.5	76.0	82.0
8	67.0	73.0	80.5
9	66.5	72.5	78.0

10	66.0	71.0	74.5
11	65.0	67.5	71.0
12	63.0	66.0	69.0
13	61.5	64.0	68.5
14	60.5	63.5	67.5
15	58.0	62.0	66.0

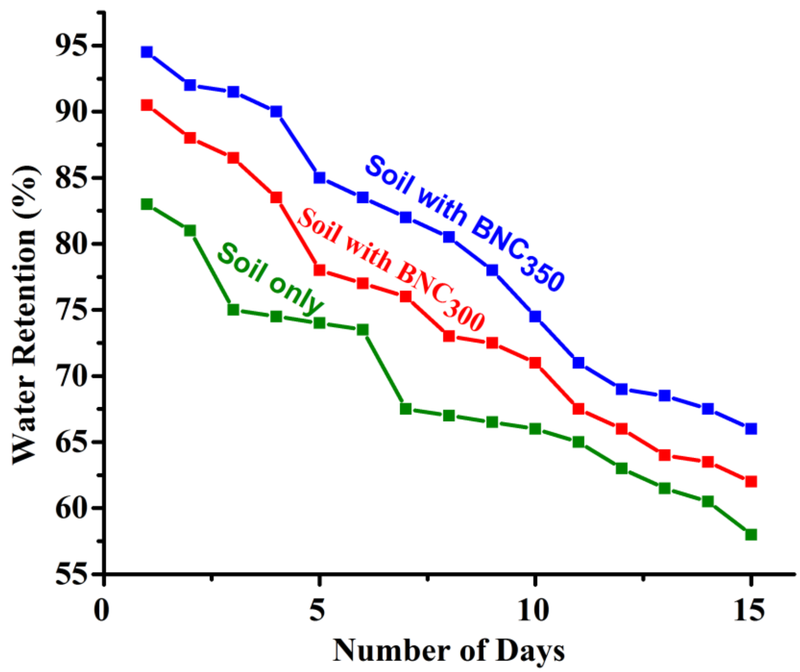


Figure 23: Curve of all three Values of $WBNC_{350}$, $WBNC_{300}$ in contrast to Soil (no char) for the water retention studies

4.2.5. Slow Release Studies of BNC

The tailored BC was studied using normal tap water for its slow release capabilities. Figures 24-27 portray the graphs & performance of the different nutrients in tap water over a period of ten days. Parameters like size of the pores of the biochars, adsorption/desorption of the different nutrients have a critical part in liberation of the macro-micro salts ions. From the Data, for each of the 4 micro (Na_2O) and macro (NO_3^-

[1] , K_2O & P_2O_5) salts the liberation was somewhat quick at the commencement of every process nevertheless with increased time the pattern then started getting an approximately steady curvature at the final steps of the experiments. This presentation is in matching with the nutrient consumption version of the crops which wants higher minerals and salt ions within the developing degrees of the vegetation and when they sprout then that crop or plant requires a regular resource of diverse macro-micro nutrients to enhance their growth and boom while improving their productivity.

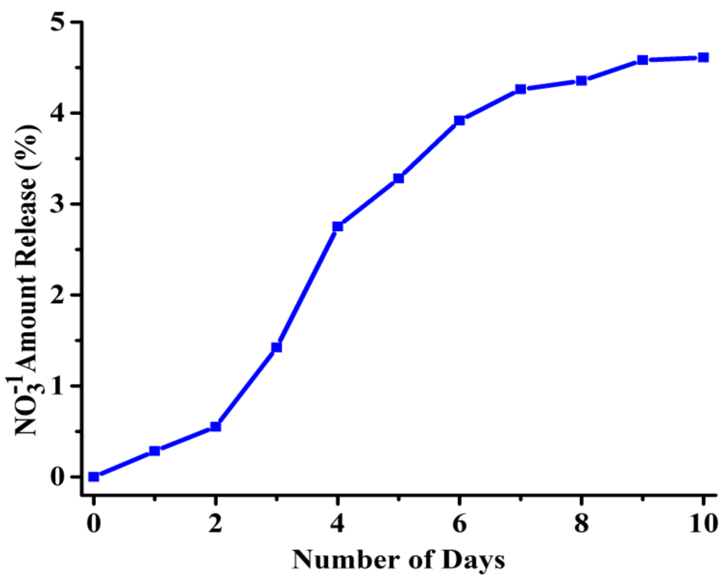


Figure 24: Nutrient Release Curve of Nitrate in Tap water in nano-char

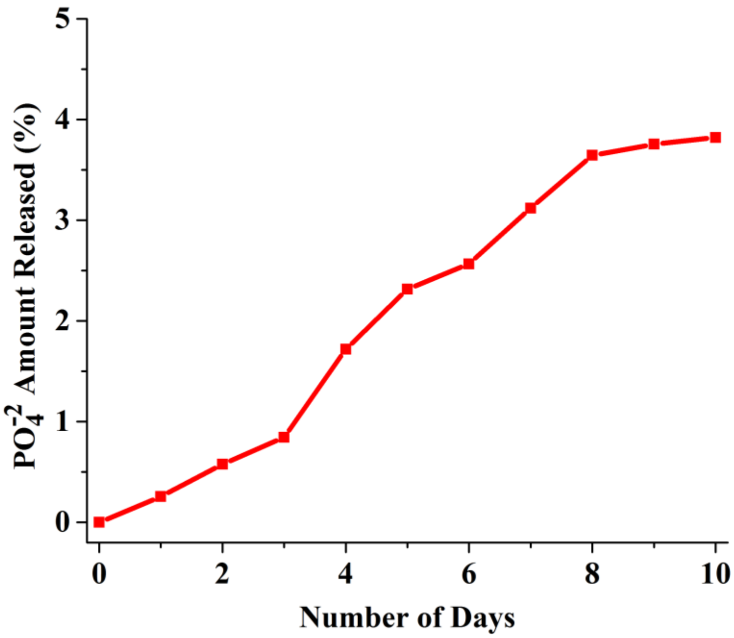


Figure 25: Nutrient Release Curve of Phosphate in Tap water in nano-char

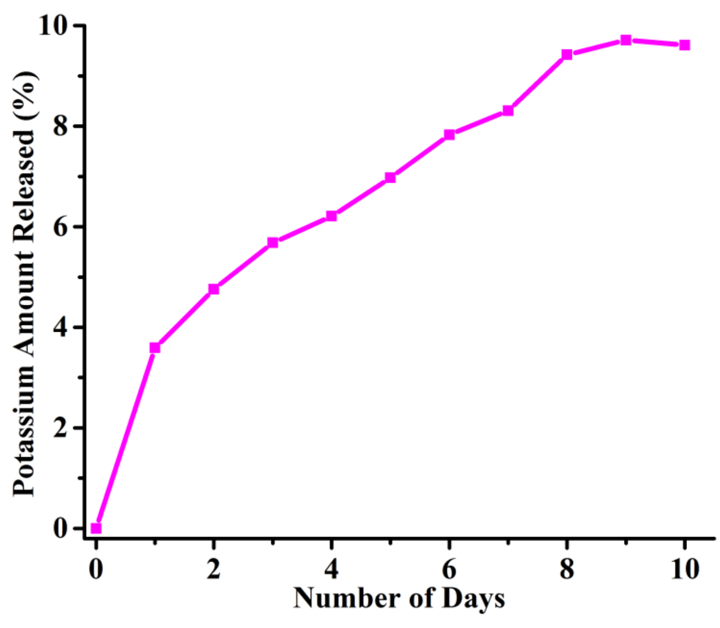


Figure 26 : Nutrient Release Curve of Potassium in Tap water in nano-char

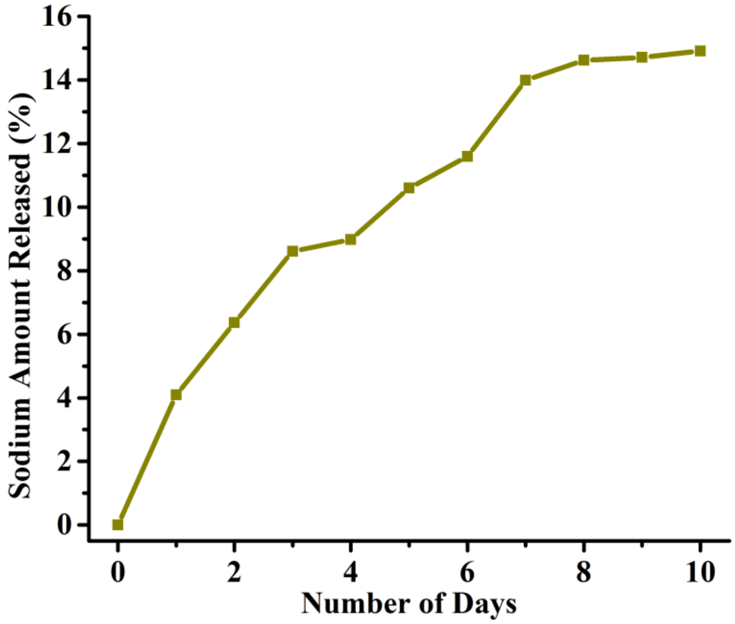


Figure 27: Nutrient Release Curve of Sodium in Tap water in nano-char

Conclusion

Wheat Straw was pyrolyzed producing BC which was further modified and synthesized into Nano-Biochar. Both samples were impregnated via nutrients. Overall final data showed both samples to be neutral or near to neutral pH and a spongy porous arrangement which was confirmed through the snapshots of SEM where as the EDX results corroborate impregnation of the diverse macro & micro salt ions inside the core of the biochars. FTIR confirmed different functional group among the samples where are TGA showed the thermal stability of all the biochars. Also the analysis via BET confirmed the micro-porous and meso-porous structure of the biochar samples. Experiments were also carried out to find parameters such as salt index of the biochar, slow release of the BNC, water retention & absorbance studies. Common points proved Nano-char to have excellent potential and be used as sustainable product while nano-char produced at 350 °C prove greater potential outcomes , hence both BNC's could used to enhance plant health and vegetation through offering excessive content of vitamins-nutrients & for prolonged time, Low salt index and good pH guarantees that soil fertility could also be upgraded by using the BNC whereas using waste agricultural to produced organic fertilizers also help in mitigating the recent environmental issues around the globe. More over this also ensure that waste agriculture is managed and that more useful products are produced from it decreasing land contamination otherwise. Finally, they can also be produced economically and are eco-friendly which can play a completely specific and essential function in the future of sustainable agriculture.

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